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Influence of cooling rate on the properties of ferromagnetic shape memory alloy

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Abstract Polycrystalline $Co_{45}Ni_{25}Ga_{30}$ alloys were prepared by arc melting method, followed by the quenching separately into liquid nitrogen, ice cold water and air, respectively The powder X-ray diffraction pattern of slow cool alloys showed a mixed phase structure, whereas the quenched alloys revealed a single phase structure No marked structural difference was observed in the X-ray diffraction patterns of the air cooled, ice quenched and liquid nitrogen quenched samples However, the martensitic and austenite transformation parameters observed by Differential scanning calorimeter (DSC) showed appreciable change in quenched samples The slow cooled sample did not show any signature of martensitic transformation The surface relief due to martensitic transformation was observed in optical microscope for all three quenched samples The thickness of the twin lines increased for samples cooled at higher rates The Curie temperature of the three samples shows subtle variations

Keywords Martensite, Curie temperature

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1. Introduction

Ferromagnetic shape memory alloys (FSMA) are excellent candidates for magnetic actuator applications since one can invoke large strain in them either through the martensitic transformation or rearrangement of martensite variants induced by an external magnetic field. The observation of up to 5.7% magnetically induced shear strain in Ni-Mn-Ga [1] has intensified the search for other alloys exhibiting FSMA behavior. Co-Ni-Ga [2] and Co-Ni-Al [3] FSMAs have recently attracted attention due to their good ductility, lower cost and stability in preparation. Co-Ni-Ga alloys have a wide range of martensitic transformation temperatures and Curie temperatures, which are both sensitive to alloy composition. The normal procedure for preparation of these alloys involves preparation of the master alloy

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ingots by arc melting (or induction melting) followed by homogenization at high temperature and quenching into cold temperature. This is done to retain a high temperature phase at room temperature and escape some intermediate phase normally present in the system In our knowledge, no systematic study on the influence of the cooling rate on the properties of these alloys has been carried out. A Differential Scanning Calorimetric study of $Co_{45}Ni_{25}Ga_{30}$ along with Curie temperature (T_C) of alloy quenched at different cooling rates is reported here.

2. Experimental details

Polycrystalline ingots (5g weight) of $Co_{45}Ni_{25}Ga_{30}$ alloys were prepared by arc melting appropriate amounts of high purity elemental powders of Co (99 9+%, 100 mesh, Aldrich) Ni (99.99%, 100 mesh, Aldrich) and Ga (99.99%, NFC, India) under argon atmosphere, homogenized at 1423K for 4 hrs and slowly cooled inside the furnace under a pressure ~10^{-5} mbar. Three small discs were cut out from the slow cooled alloy, sealed in three different fused silica ampoules at a pressure ~10^{-5} mbar, annealed at 1423K for 4 hours and then quenched separately into liquid nitrogen, ice cold water and air, respectively In this manner, three alloys were prepared under different cooling rates Powder X-Ray diffraction (XRD) studies were performed on the three alloys using Seifert 3003 T/T XRD (Cu K_α = 1.5406 Å). The thermal studies were performed using a differential scanning calorimeter (DSC PerkinElmer DSC7) at a constant heating/cooling rate of 20°C/minute The surface morphology of the alloys was observed using an optical microscope (Zeiss KS 300) in reflection mode. An indigenously developed low-field ac susceptometer (ACS) was used to determine the ferromagnetic to paramagnetic transition (Curie) temperature (T_C).

3. Results and discussion

XRD patterns (Figure 1) of both the ice water and liquid nitrogen quenched samples had six Bragg reflections at same 2θ values All six reflections in Figure 1 were indexed to

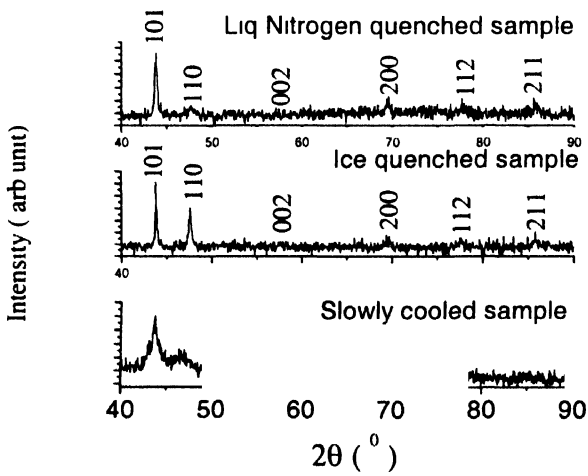

Figure 1. XRD pattern of $Co_{45}Ni_{25}Ga_{30}$ alloys

a body centred tetragonal structure corresponding to a single martensite phase The calculated lattice constants are $a = b = 2.72$ Å, $c = 3.23$ Å The powder X-ray diffraction pattern of slow cooled alloys showed a mixed phase structure The extra peaks present at $2\theta \approx 51^{\circ}$ in the XRD pattern is due to the presence of some other phase in the slowly cooled alloy.

The DSC curves of the two quenched samples are shown in Figure 2. The endothermic peak on the heating cycle and the exothermic peak on the cooling cycle correspond to the structural phase transitions from martensite-austenite (M→A), and austenite-martensite (A→M) phases, respectively. The starting temperature of martensitic transformation (M_s), the finishing temperature of the forward transformation (M_f), the starting temperature of the reverse martensitic transformation (A_s) and the finishing temperature of the reverse transformation (A_f) are indicated in Figure 2. The transformation parameters, namely, M_s, M_f, A_s, A_f and the enthalpy involved in the transformations (ΔH_A and ΔH_M) are listed in Table 1. No evidence of M→A and/or A→M transformations was observed in slowly-cooled sample. This indicates that the martensite phase could be formed in this alloy only by rapidly cooling the homogenized master alloy.

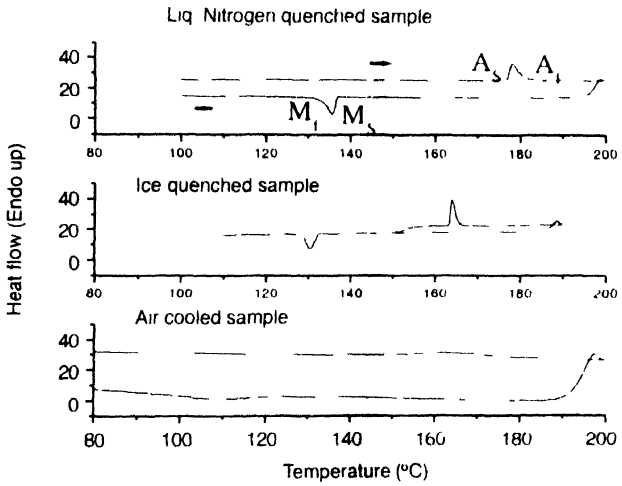

Figure 2. DSC curves of $Co_{45}Ni_{25}Ga_{30}$ alloys

Analysis of the DSC data of the air cooled, ice quenched and liquid nitrogen quenched alloys showed higher A_s and A_f temperatures in liquid nitrogen quenched sample. When samples were quenched from a high temperature to a very low temperature suddenly, the elastic energy of the system can not dissipate by any other way. Thus the system accumulate (self accumulation of martensite) the elastic energy by displacive transformation of the lattice points. Thus higher quenching rate introduces more elastic energy (or density of dislocation) in the system. To change from martensite state to austenite state it has to overcome more elastic energy and hence the transformation temperatures are higher for samples with higher quenching rate. In short, it can be said that higher transformation temperatures can occur due to the presence of a higher concentration of defects in the

martensite phase [4]. The same phenomena cause more thermal hysteresis. ($A_f \sim M_S$ in a highly quenched system. The elastic energy around the martensite resists the growth of the martensite unless a further driving force (*i.e.* cooling) is given [5]. The endothermic and exothermic peak of air cooled sample is very weak and wide. Thus the martensite $\leftrightarrow$ austenite transformation of air cool sample is not sharp and hence cooling rate of air cool sample is not sufficient for the formation of shape memory alloys. The martesite $\leftrightarrow$ austenite transformation of ice quenched and liquid nitrogen quenched samples are very sharp. But very high rate of quenching introduces more thermal strain into the system and cracks are developed in the bulk sample. Hence ice quenching method is more suitable for the preparation of shape memory alloys.

The surface relief due to martensitic transformation was observed in optical microscope for all three quenched samples. The thickness of the twin lines increased for samples cooled at higher rates. This is probably due to the larger displacement of lattice points to accumulate higher elastic energy for higher quenched rate sample (Liquid Nitrogen quenched). The twin lines are not distinct in the air cool sample. Moreover, some black spots were seen in the microstructure of the air cool sample. This may be due to the presence of small amounts of other intermediate phases which could not be detected in the XRD measurement.

Figure 3. Optical microscope image of $Co_{45}Ni_{25}Ga_{30}$ alloys.

Table 1. DSC data of $Co_{45}Ni_{25}Ga_{30}$ alloys.

Transformation parameter	Air cooled sample	Ice quenched sample	Liq. N_2 quenched sample
A_S (^{0}C)	148	163	177
A_f (^{0}C)	179	166	181
ΔA (= $A_f \sim A_S$)	31	3	4
ΔH_A (J/gm)	2.318	4.588	4.203
M_S (^{0}C)	124	133	137
M_f (^{0}C)	92	129	133
ΔM (= $M_f \sim M_S$)	32	4	4
ΔH_M (J/gm)	3.45	4.306	4.917
Hysteresis ($A_f \sim M_S$)	55	33	44
T_C (^{0}C)	131	119	98

The ferromagnetic to paramagnetic transition (Curie) temperature (T_C) was measured by ACS (Figure 4) and the T_C values are given in Table 1 T_C was lower for samples prepared with higher cooling rate (*i e* samples quenched in liquid nitrogen) T_C is sensitive to local crystallographic environment When the sample is quenched from high temperatures, the solidification is not under equilibrium conditions and this introduces some crystallographic defects in the sample These defects create a local disorder in their vicinity Faster cooling rates introduce more defects in the sample Thus the degree of disorder in the sample prepared by quenching in liquid nitrogen is more than in the other two samples The increased crystallographic disorder results in decreased grain size in polycrystalline materials T_C value show a tendency to shift to lower temperatures with the reduction in grain size similar results have been reported in rapidly solidified Nd-Fe-B samples [6] Hence, lower T_C values observed in the present work for samples prepared with higher quenching rate is in line with the earlier reports on other rapidly solidified ferromagnetic materials

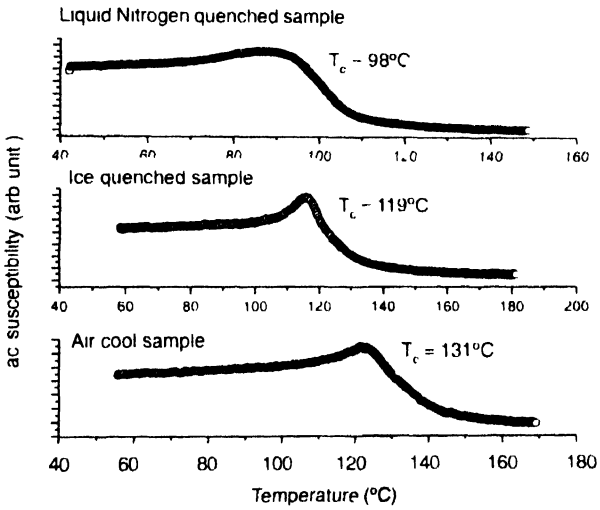

Figure 4 Variation of ac susceptibility of $Co_{45}Ni_{25}Ga_{30}$ alloys with temperature

4. Conclusions

$Co_{45}Ni_{25}Ga_{30}$ alloys exhibiting M→A and/or A→M transformations were formed by rapidly cooling the homogenized master alloy in air, ice water or liquid nitrogen Structurally, the alloys prepared under different cooling rates exhibited a single martensite phase However, the thermal transformation behavior of these alloys observed using a DSC showed marked differences Air cool alloys does not exhibit sharp M→A and/or A→M transition and very high rate of quenching (liquid nitrogen quenched) may develop cracks in the bulk sample Thus the ice quenched sample is the best among these samples for shape memory application. Moreover, the ice quenched alloy is ferromagnetic in its martensite phase for a large temperature range (T_C = 119 ^{0}C) Thus it can be considered as a potential candidate for ferromagnetic shape memory alloy applications

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